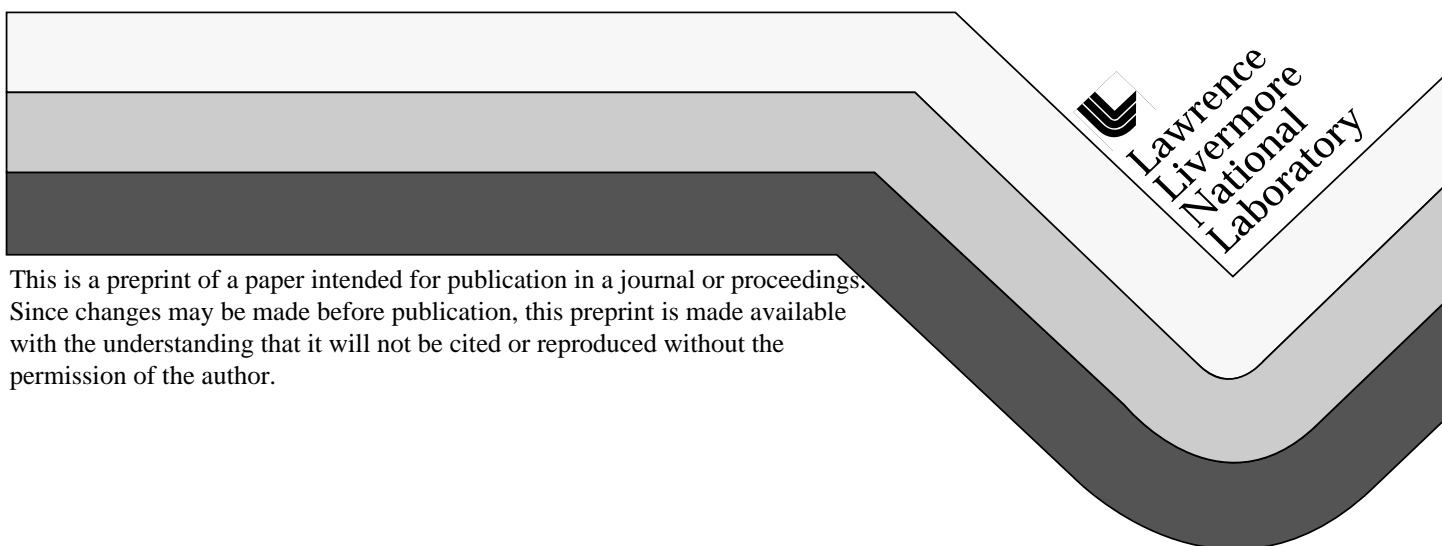# World-Wide Redistribution of ^{129}Iodine from Nuclear Fuel Reprocessing Facilities Results from Meteoric, River, and Seawater Tracer Studies

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WORLD-WIDE REDISTRIBUTION OF ^{129}IODINE FROM NUCLEAR FUEL REPROCESSING FACILITIES: RESULTS FROM METEORIC, RIVER, AND SEAWATER TRACER STUDIES

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Abstract

Releases of the long-lived radioisotope of iodine, ^{129}I from commercial nuclear fuel reprocessing facilities in England and France have surpassed natural, and even bomb test inventories. ^{129}I/^{127}I ratios measured in a variety of environmental matrices from Europe, North America and the southern hemisphere show the influence of fuel reprocessing-derived ^{129}I, which is transported globally via the atmosphere. Transport and cycling of I and ^{129}I in the hydrosphere and in soils are described based on a spatial survey of ^{129}I in freshwater.

1. INTRODUCTION

The database for iodine (^{127}I) and the ratio of ^{129}I/^{127}I in natural materials is relatively small, and highly scattered, owing to inherent variability for different rock and water types, and to difficulties in the measurement of both the concentration and isotope ratio. Iodine concentrations in surface waters are quite low in general, and measurement of ^{129}I/^{127}I ratios in iodine from natural materials is by accelerator mass spectrometry, available at only a few laboratories worldwide. We made a spatial survey of ^{129}I/^{127}I ratios and stable iodine concentrations in freshwater and seawater, in order to determine sources of ^{129}I.

Given the geochemical behavior of iodine, which is generally conservative as an anion, but has an affinity for organic material; and the steep increase of ^{129}I due to fuel reprocessing emissions, ^{129}I is a good candidate for a hydrologic and biogeochemical tracer on a global scale. The long-lived isotope of iodine, ^{129}I (half-life 15.6 m.y.), is produced naturally in the atmosphere by the interaction of high-energy cosmic rays with xenon isotopes. Beginning in about 1945, and peaking in 1963, nuclear bomb tests added tens of kilograms of ^{129}I to the atmosphere, resulting in ^{129}I/^{127}I ratios several orders of magnitude higher than natural ratios [1, 2]. Unlike most radionuclides produced during atmospheric bomb testing which have returned to near pre-nuclear levels, the amount of ^{129}I in the atmosphere and in surface waters has continued to increase due to releases from nuclear fuel reprocessing facilities. ^{129}Iodine releases into the North Sea from two such fuel reprocessing facilities (at Sellafield, England and Cap de La Hague, France) continue at very high levels [3], providing in effect, a point source for the total surface inventory.

The total natural ^{129}Iodine in the surface environment was about 80 kg (5×10^{-4} kg in the atmosphere). For comparison, atmospheric bomb tests produced 45 kg [3], and the Chernobyl reactor accident released 1.3 kg [1]. On a larger scale, the facilities at Sellafield and La Hague have cumulatively released 1440 kg since operations began in the late sixties [3]. As of 1994, direct ^{129}I releases from the facilities at Sellafield and LaHague into the ocean were about 200 kg/yr, with a steep increase from the LaHague facility from about 1990 and continuing to the present [3]. Iodine is a volatile, atmophile element. McKay et al. [4] give evidence that the method of trapping off gases at the Sellafield facility allows 3-6% of the ^{129}I produced to be released in gaseous discharges. If conditions were similar at the Cap de LaHague facility, that would indicate total releases of 6-12 kg/yr to the atmosphere from both facilities combined. Another estimate based on measurements of iodine activity in the air near the Sellafield plant, puts this figure at 9% (or 18 kg/yr; [5]).

Releases of [129]I to the atmosphere allow for long-range transport, given the relatively long residence time of iodine in the atmosphere, and its high degree of reactivity. The [129]I transported atmospherically is deposited on the continents by (mainly wet) deposition, where it infiltrates soil, is taken up by plants, and is washed into rivers and other surface water bodies. Potential applications of [129]I as a tracer include: dating recently recharged groundwater, tracing sources of salt in river watersheds, tracing and dating post-nuclear terrestrial organic material in the nearshore marine environment, tracing atmospheric transport and deposition of iodine, and defining the spatial extent of the influence of fuel reprocessing emissions.

2. METHODOLOGY

A thorough description of the method of extraction of I from water samples can be found in Ref. [6]. Iodine concentrations in raw water samples and in extracts were measured by inductively coupled plasma mass spectrometry or by ion chromatography. [129]I/[127]I ratios were measured by AMS at Purdue University's PRIME Lab. Procedures for running [129]I are described in Ref. [7]. Because the ratios measured for water samples were all $> 5.0 \times 10^{-12}$ (well above the detection limit of 5×10^{-15}), errors due to counting statistics in the detector are relatively small, and 1 sigma errors are <10%. Procedural blanks are $.07 - 0.5 \times 10^{-12}$, which were in the range expected for the carrier iodine, and therefore no corrections to the measured ratios were made for blanks.

3. RESULTS AND DISCUSSION

Stable iodine concentrations and [129]I/[127]I ratios are shown graphically in Figs 1-3. In all locations and in all matrices examined, there is evidence for [129]I levels in excess of what is expected from bomb fallout alone. This is most evident in meteoric water samples, where relatively rapid cycling takes place, and where there is relatively little dilution by stable iodine.

The [129]I that is released directly into the atmosphere from the fuel reprocessing facilities clearly is not distributed evenly over the globe. [129]I/[127]I ratios measured in epiphytes within 60 km of the Sellafield site were 15 to 6693×10^{-8} [8], two to four orders of magnitude higher than ratios measured in Germany and other parts of Europe [9]. Our ratio for meteoric water from Sauverny, France (near Geneva, Switzerland) is the highest in Fig. 1, and is more than an order of magnitude greater than all but two samples measured in the U.S. In order to estimate the amount of fuel-reprocessed [129]I potentially distributed great distances from the fuel reprocessing facilities in Europe, we calculate the "standing crop" of [129]I in the atmosphere over the continental U.S., and extrapolate to the northern hemisphere. A conservative estimate of the residence time of total iodine in the atmosphere is 14 days [10]. Using a global precipitation rate of 4.96×10^{17} kg/yr and our median stable iodine concentration in rain of 1.7 ng/ml, one calculates a flux of iodine from the atmosphere of 8.4×10^8 kg/yr. The median [129]I/[127]I ratio measured in rainwater for U.S. locations is approximately 2100×10^{-12}. Here it is important to note that 80% of atmospheric radioiodine deposition (at mid-latitudes with about 1 m/yr of rainfall) occurs during precipitation events; 20% by dry deposition [11]. Assuming no inter-hemispheric mixing, and using the median ratio, mass of [127]I in the atmosphere, and 14 day residence time, the mass of [129]I in the atmosphere at any given time is 0.04 kg. The roughly calculated 0.04 kg can be compared with 0.7 kg (again using the 14 day mean residence time) of the estimated 18 kg/yr released from Sellafield and LaHague in the atmosphere at any given time. Given the great distance between the source and the continental U.S., the fact that approximately 6% of the estimated atmospheric releases reaches the sampling area seems reasonable.

As fine aerosols or in gaseous forms, [129]I can be mixed from top to bottom of the troposphere very quickly (< 1day). Global tropospheric circulation patterns are such that in winter months, the air mass over northern Europe is transported by strong winds in an easterly-north-easterly direction. However, during summer months, there is a significant wind component that drives the air mass to the south, along the western edge of Africa, and across the Atlantic via the trade winds. Both of these
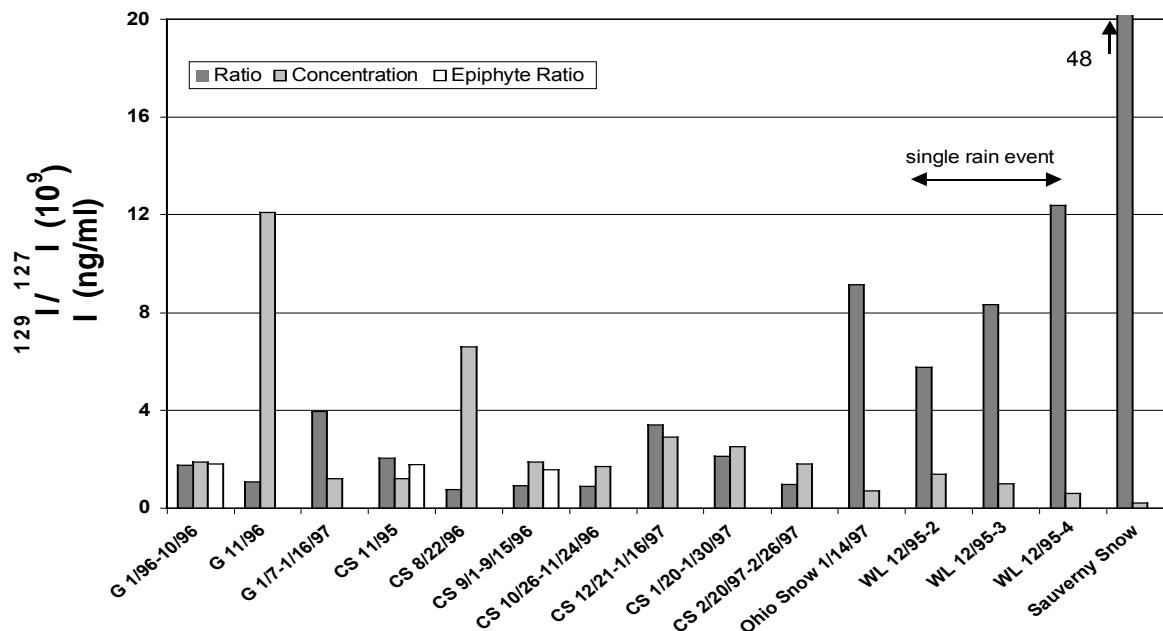
FIG. 1. Meteoric water and selected epiphyte iodine concentrations and $^{129}I/^{127}I$ ratios [6]. Sample locations, on x axis, are arranged from coastal locations (left) to inland (right). Sample locations are: G-Galveston, Texas; CS-College Station, Texas; Mansfield, Ohio; WL-West Lafayette, Indiana; Sauverny, France.

circulation patterns could result in transport of ^{129}I from European fuel reprocessing facilities to the continental US.

3.1 Rivers

$^{129}I/^{127}I$ ratios measured in river waters range over 4 orders of magnitude, from 76×10^{-12} to $850,000 \times 10^{-12}$. Immediately obvious are rivers with point sources for ^{129}I in their watersheds (Fig. 2). These include the Savannah River, with the Savannah River Plant upstream from the sampling location, and the Columbia River, with the Hanford Facility upstream of the sampling site. Several studies have shown that these sites have had purposeful and accidental releases [12, 13] of radionuclides, including ^{129}I. Interestingly, two rivers near those directly affected by point source runoff are indirectly affected, most likely by atmospheric releases. The Altamaha River, in northern Georgia does not drain the Savannah River Plant area but still has a greatly elevated $^{129}I/^{127}I$ ratio. Likewise, the Hood River, a tributary to the Columbia, downstream from Hanford, has a ratio much higher than rivers of similar iodine concentration. In these two cases, historical releases of ^{129}I to the atmosphere [12, 13] have resulted in elevated levels of ^{129}I in watershed soils and plants, and this ^{129}I has been subsequently transported to the rivers during runoff.

We attribute the high ratios and ^{129}I concentrations observed in two European rivers (i.e., the Rhone and Rhine Rivers) to the proximity of the main source for ^{129}I, *viz.* the nuclear fuel reprocessing facilities at Sellafield, England and at Cap de la Hague, France. These elevated levels must likewise be due to atmospheric emissions and rainout followed by runoff, since liquid releases go directly to the English Channel. The ratio measured in the Rhine River is somewhat lower than the ratio measured in the snow from France, while the Rhone River had a much higher ratio. These variations are likely due to spatial variations in atmospheric re-distribution and fallout of fuel reprocessing ^{129}I.
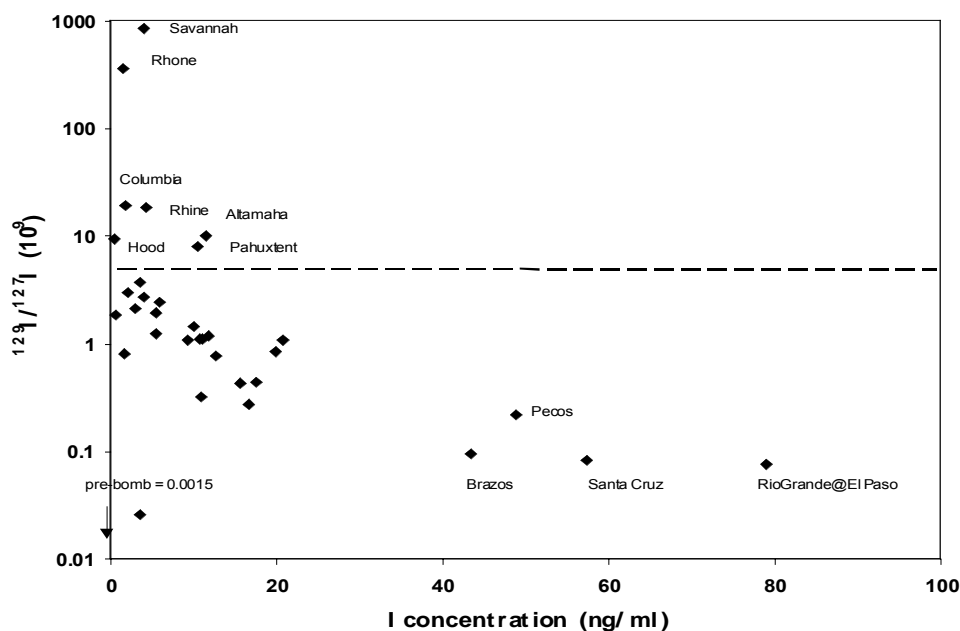
FIG. 2   Results from a spatial survey of (mainly North American) rivers. Rivers with point sources in their watershed (above dotted line) have greatly elevated ratios compared to those affected only by global dispersal of fuel reprocessing-derived ^{129}I (below).
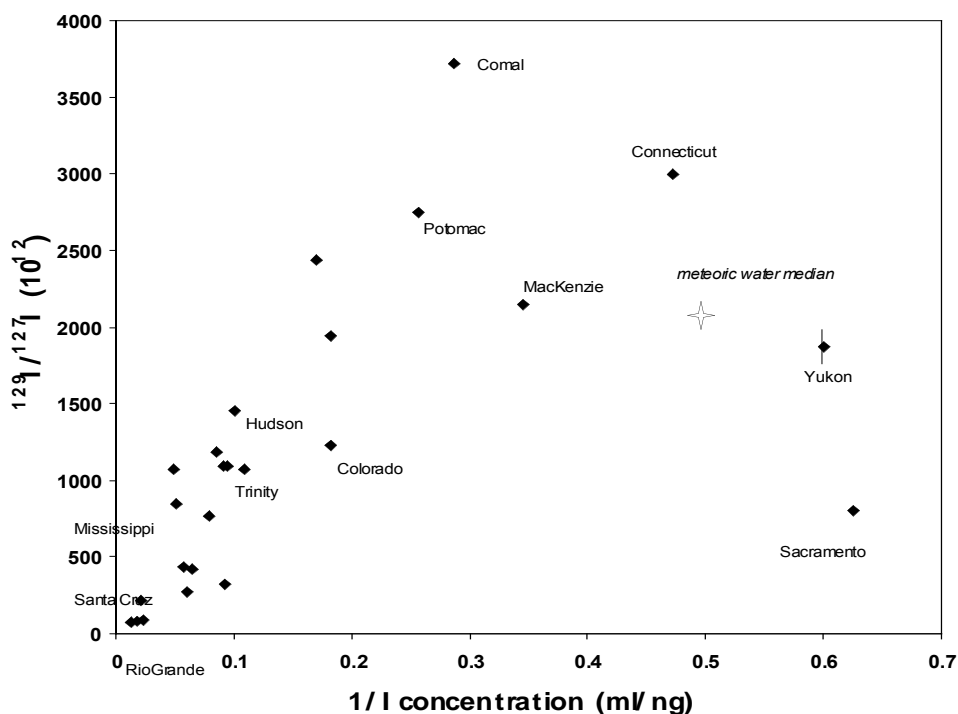

FIG. 3. Mixing diagram for rivers not affected by local point sources for ^{129}I. Possible mixing between atmospheric and soil-derived endmembers is evident. A representative 1σ error bar is shown (Yukon).

All ^{129}I/^{127}I ratios and ^{129}I concentrations observed in other rivers, i.e., those outside the range of influence of point sources are still elevated above levels attributable solely to bomb fallout. Consider for example, for the Mississippi River watershed, with a drainage area of 3.27×10^{12} m^2. Using a cumulative bomb fallout of 7.5×10^{11} atoms ^{129}I/m^2 [14] and a residence time of iodine in soil of 100 yr [12, 15], one calculates a flux of 2.5×10^{22} atoms/yr into the Mississippi River from watershed soils. The measured river concentration of 8×10^7 atoms/kg and flow rate of 5.8×10^{14} kg/yr, provides a flux nearly twice as high, 4.6×10^{22} atoms/yr. Addition of older, lower ratio iodine from watershed soils tends to reduce ratios in river water below those found in rainwater.

Figure 3 is a mixing diagram for rivers other than those affected by local sources, as discussed above. A two component mixing trend is evident. End members are an atmospheric component, with a broad range of values, and a soil leachate component with a high iodine concentration and pre-bomb ratio (1.5×10^{-12}; [16]). The atmospheric component varies considerably, due to unevenness in the rainout. Stable iodine concentration in rain depends (weakly) on distance from the coast, and on the chemical form of the iodine. ^{129}I and ^{127}I are not well mixed in the atmosphere, nor should we expect them to be given their disparate sources. Accordingly, in rivers which plot within and near the atmospheric end member oval, meteoric (oceanic) cyclic salt provides the main source of iodine, and atmospheric emissions from nuclear fuel reprocessing represent the main source of ^{129}I. The Connecticut, Yukon, MacKenzie, and Potomac Rivers are among this type of river. While these rivers have been categorized as having a larger component of cyclic salt than the average world river [17], for most constituents they are still rock-dominated. Because iodine is relatively much less abundant in rock-forming minerals, the cyclic salt component of iodine assumes greater significance.

Rivers with high iodine contents (e.g., the Rio Grande, the Pecos, and to a lesser extent the Mississippi and southeastern USA rivers) show some affect by anthropogenic ^{129}I in their iodine isotope ratios, but show a component of pre-anthropogenic ^{129}I. The rivers with the highest I concentrations have watersheds in arid regions where and water use is very high. Over the past several decades, the salt content of these rivers has increased dramatically, mainly due to non-point source runoff and return flow from cultivated fields. In these agricultural areas, high evapo-transpiration and inefficient irrigation techniques combine to disturb the natural salt balance in soils. In addition, contributions of iodine from fertilizers, herbicides, pesticides, and from certain crops, which may concentrate iodine, should also be considered [18]. Because pre and post-bomb atmospheric ^{129}I/^{127}I ratios differ by 3 orders of magnitude, addition of a small fraction of anthropogenic iodine can raise the measured ratio substantially.

3.2 Comparison with seawater

The high ratios observed in rivers indicate a significant worldwide flux of ^{129}I off the continents into the oceans; about 0.5 kg/yr. However, 30 years accumulation of this flux, all in the ocean's mixed layer (top 100m), would result in a seawater ratio of 5×10^{-12}; much lower than that observed. Measurements of ^{129}I/^{127}I ratios in seawater in areas distant from Sellafield and La Hague include those by Santschi et al. [19] in the mid-Atlantic Bight, and Schink et al. [20] in the Gulf of Mexico. Ratios near the surface are 107×10^{-12} and 67×10^{-12}, respectively. Another profile from the Gulf of Mexico taken in 1996, but prepared by the method of chemical extraction described above, gave similar results, with a maximum ratio of 95×10^{-12}. While these ratios are about an order of magnitude lower than those observed in most rivers from the adjacent continent, they are not influenced by runoff from the continent. Current-born transport of fuel reprocessing ^{129}I from the North Sea comprises the majority of the ^{129}I measured in seawater even in locations remote from the source.

3.3 ^{129}I in the Southern Hemisphere

Almost all nuclear activities are restricted to the northern hemisphere: all declared and threshold nuclear powers, the entire reprocessing capacity and more than 99% of the nuclear power production are located in the northern hemisphere. Investigation of the presence of ^{129}I in the Southern Hemisphere is

thus a good test for the global transport of this isotope. We are in the process of collecting a representative set of samples from the southern continents, but have data so far from lakes in Australia and New Zealand. The ^{129}I concentrations found for Australia and New Zealand are quite similar, from 10^{-10} to 10^{-9}, with the New Zealand values at the lower end of this range. Although the database is still very limited, these observations suggest that ^{129}I concentrations are in general lower by one order magnitude than in the northern hemisphere (but still significantly above pre-bomb levels) and that ^{129}I concentrations and ^{129}I/^{127}I ratios are above the levels expected for fallout from atmospheric testing.

REFERENCES

[1] PAUL, M. et al., Measurement of ^{129}I concentrations in the environment after the Chernobyl reactor accident, Nucl. Inst. Meth. Phys. Res. **B 29** (1987) 341-345.

[2] MURAMATSU, Y., OHMONO, Y., Iodine-129 and Iodine-127 in environmental samples collected from Tokaimura/Ibaraki, Japan, Sci. Tot. Environ. **48** (1986) 33-43.

[3] RAISBECK, G.M. et al., ^{129}I from nucelar fuel reprocessing facilities at Sellafield (U.K.) and La Hague (France); potential as an oceanographic tracer, J. Mar. sys. **6** (1995) 561-570.

[4] MCKAY, H.A.C. et al., Management of iodine-129 from reprocessing plants, Radioactive Waste Management **5** (1984) 81-102.

[5] UNSCEAR, Sources, Effects, and Risks of Atomic Radiation. U.N. Committee on the Effects of Atomic Radiation, (1988).

[6] SHARMA, P. et al., The ^{129}I program at PRIME Lab, Nucl. Inst. Meth. Phys. Res. **B 123** (1997) 347-351.

[7] MORAN, J.E. et al., Atmospheric dispersal of 129Iodine from European nuclear fuel reprocessing facilities, Environ. Sci. and Tech. (submitted).

[8] RUCKLIDGE, J. et al., ^{129}I in moss down-wind from the Sellafield nuclear fuel reprocessing plant, Nucl. Inst. Meth. Phys. Res. **B 92** (1994) 417-420.

[9] HANDL, J. Concentrations of ^{129}I in the biosphere, Radiochim. Acta **72** (1996) 33-38.

[10] RAHN, K.A. et al., Tropospheric Halogen Gases: Inorganic and Organic Components, Science **192** (1976) 549-550.

[11] SANTSCHI, P.H. et al., Chernobyl Radionuclides in the Environment: Tracers for the Tight Coupling of Atmospheric, Terrestrial, and Aquatic Geochemical Processes, Environment **22** (1988) 510-516.

[12] BOONE, F.W. et al., Residence half-times of ^{129}I in undisturbed surface soils based on measured soil concentration profiles, Health Phys. **48** (1985) 401-413.

[13] BRAUER, F.P., RIECK, H.G.J. ^{129}I, ^{60}Co and ^{106}Ru Measurements on Water Samples from the Handford Project Environs' Report no. BNWL-SA-4478, Battelle Pacific Northwest Laboratories, Richland, Washington, USA (1973).

[14] WAGNER, M.J.M. et al., Increase of ^{129}I in the environment, Nucl. Inst. Meth. Phys. Res. **B 113** (1996) 490-494.

[15] ROBENS, E. et al., Iodine-129 in the environment of a nuclear fuel reprocessing plant. IV. ^{129}I and ^{127}I in undisturbed surface soils, J. Environ. Radioactivity **9** (1989) 17-29.

[16] MORAN, J.E. et al., ^{129}I/^{127}I ratios in Recent marine sediments: Evidence for a fossil organic source component, Chem. Geol. (in press).

[17] GIBBS, R.J., Mechanisms controlling world water chemistry, Science **170** (1970) 1088-1090.

[18] WHITEHEAD, D.C., Studies on Iodine in British Soils, J. Soil Sci. **24** (1973) 260-270.

[19] SANTSCHI, P.H. et al., Evidence for elevated levels of Iodine-129 in the Deep Western Boundary Current in the Middle Atlantic Bight, Deep Sea Res. **43** (1995) 259-265.

[20] SCHINK, D.R. et al., ^{129}I in Gulf of Mexico Waters, Earth Planet. Sci. Lett. **135** (1995) 131-138.